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## Matrix-Assisted Synthesis of Palladium Nanocage and Nanowires

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### ABSTRACT

Our study describes the synthesis of novel nanoscale Pd cage and wires whose sizes and shapes are templated by mesoporous matrices. The templates used are cubic phase MCM-48 and hexagonal phase C<sub>n</sub>MCM-41 (n = 16, and 22), SBA-15, which have pore diameters of ~3, ~3.8, ~4.7, and ~9 nm, respectively. For Pd@MCM-48, the Pd metal forms spherical domains (~38 nm) consisting of three dimensionally interconnected into Pd arrays; for Pd@SBA-15 and Pd@MCM-41, the Pd metal forms of one-dimensional wires. Etching out the matrix produces porous Pd cages (pore sizes of ~1.5 - 2.0 nm) with retaining original domain sizes of ~38 nm; similarly Pd@SBA-15 and Pd@MCM-41 afford freestanding Pd nanowires. All the materials are examined by TEM, XRD, BET, and EDAX analysis. Furthermore, the thermal behavior of Pd nanowire is briefly described.

### INTRODUCTION

Recently, interest has grown in the synthesis of nanosized materials due to their novel electronic, optical, and catalytic properties [1]. Of the various methods available to prepare these materials, one is the templated synthesis where the desired nanomaterial is encapsulated into the channels and pores of a host [2]. Mesoporous solids with pore size tunability ranging from ~2 to ~30 nm have been the focus of special attention as hosts for quantum dots and wires [3]. One of the studies used the two step nanocasting process where mesoporous organic networks were grown by polymerization of monomers and subsequent removal of silicate matrix [4]. Excellent carbon-based mesoporous materials were also obtained from a MCM-48 template [5]. The fabrication of stable metallic structures with ordered nanopores of less than 10 nm are rare and have recently been reported for Ag, Pt, and Sn [6]. Using the mesoporous silica template, it is potentially feasible to have various 1 to 3 dimensional shapes of nanostructured materials depending on the architecture of the silicate host. For example, recently, Stucky and coworkers reported the preparation of Au, Ag, and Pt nanowires using hexagonal mesoporous silica (SBA-

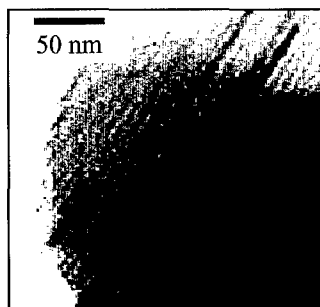
15) via a solution phase infiltration process [7]. Ordered porous gold nanostructures with larger pore dimensions ( $\sim 150$  nm –  $1$   $\mu$ m) have been synthesized by using latex spherical templates [8]. We present in this report matrix free palladium based porous nanoballs and nanowires as well as palladium superlattices and wires inside of cubic MCM-48 and hexagonal MCM-41 and SBA-15 matrices. Pd was chosen as the case study material because of its catalytic activity and its potential applications in  $H_2$  storage and advanced electronics [9].

## EXPERIMENTAL DETAILS

Matrix materials such as MCM-48 (pore size of  $\sim 3$  nm),  $C_{16}$ MCM-41,  $C_{22}$ MCM-41, and SBA-15 (pore size of  $\sim 3.7$ ,  $\sim 4.6$ , and  $\sim 9$  nm) particles are dried at  $400$   $^{\circ}$ C for  $8$  h under dynamic vacuum ( $\sim 10^{-2}$  Torr) [10], prior to introduction of the Pd metal-organic precursor,  $Pd(hfac)_2$  ( $hfac=1,1,1,5,5,5$ -hexafluoroacetylacetonate) via chemical vapor infiltration (CVI) [11]. The precursor is sublimed into the empty pores of the mesoporous materials under vacuum ( $\sim 10^{-2}$  Torr) at  $55$   $^{\circ}$ C; during this time the samples exhibit a color change from white to the yellow color indicative of the precursor [12]. The resulting  $Pd(hfac)_2@MCM-48$ ,  $Pd(hfac)_2@C_{16}MCM-41$ ,  $Pd(hfac)_2@C_{22}MCM-41$ , and  $Pd(hfac)_2@SBA-15$  composites are then pyrolyzed at  $150$   $^{\circ}$ C under a  $10\%$   $H_2/N_2$  flow to produce black powders of  $Pd@MCM-48$ ,  $Pd@C_{16}MCM-41$ ,  $Pd@C_{22}MCM-41$ , and  $Pd@SBA-15$ . To obtain unsupported freestanding Pd nanocage and nanowires, the Pd containing silicate composites were carefully treated with a solution of  $HF/H_2O$ , affording a black powder suspension, which can be obtained as a black powder after centrifugation. To study the thermal behavior of the Pd nanowires, they were mounted on transmission electron microscope (TEM) grids and thermally treated under an argon atmosphere where the temperature was slowly increased at the rate of  $2$   $^{\circ}$ C/min and maintained at the designated temperature ( $150$ ,  $200$ , and  $300$   $^{\circ}$ C) for  $1$  hr and finally cooled to R. T. The sample containing grids were then transferred to TEM for analysis.

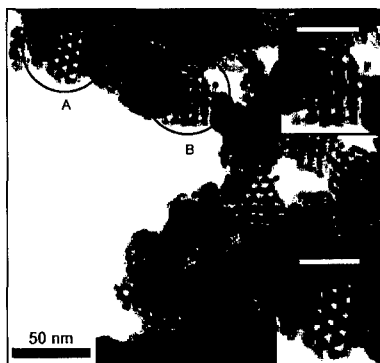
## DISCUSSION

The Pd nanowires appear as dark rod-like objects inside host matrix  $C_{16}$ MCM-41,  $C_{22}$ MCM-41, and SBA-15, respectively, and range in length from  $50$  to a few hundred nanometers. The thickness of each Pd nanowire appears to be confined by the channel diameter of the pure mesoporous silicate samples and one of the TEM image of the  $Pd@C_{22}MCM-41$  sample is show in Figure 1. This observation indicates that the silicate host frameworks were

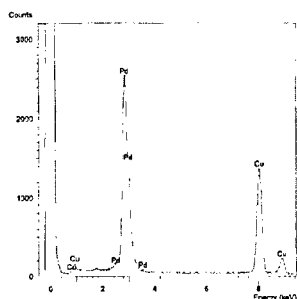


**Figure 1.** TEM images of the supported Pd nanowires within the mesoporous silicate channels: Pd@C<sub>32</sub>MCM-41.

neither deformed nor affected by the loading of Pd inside the channels by our CVI filling method. For Pd@MCM-48, the TEM images show that the Pd aggregates into ball shaped domains of 8.2 nm ( $\sigma = 3.3$ ); these domains consist of a three dimensionally interconnected network of Pd filled pores in the MCM-48 matrix. Some pore filled Pd nanoballs are clearly shown in the (111) crystallographic direction of the MCM-48 matrix. The formation of spherical ball type domains can possibly be attributed to the mesoscale stress field of periodic mesoporous structures as similarly seen in the other metal system [13]. Energy dispersive X-ray analysis (EDAX) data show Si, O, and Pd peaks and the presence of Pd as ~5 - 6 weight percent of mesoporous silicate templates.



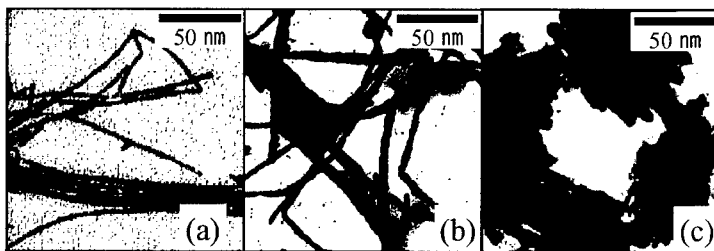
**Figure 2.** TEM image of the porous Pd superlattice nanoballs.



**Figure 3.** EDAX analysis of the Pd nanoball. Cu is from TEM grid.

To obtain freestanding Pd nanocage and wires, the silicate matrices were removed by slowly adding HF solution and the resulting black powder suspension was centrifuged to obtain the nanowires in powder form. TEM examination of the powder shows that it consists of agglomerated and randomly stacked Pd nanoballs of  $\sim 37.6$  nm ( $\sigma = 3.9$ ) in diameter. Each ball shaped domain consists of an interconnected network of Pd whose shapes and pores are obtained as the replication of the MCM-48 template (Figure 2). Some Pd nanoballs are clearly observed in the (111) and (100) crystallographic directions (Figure 2 inset). The structures of the Pd superlattices remain unchanged during the silicate dissolution process. Energy dispersive X-ray emission analysis confirms that Pd is the major product without any significant contaminants (Figure 3).

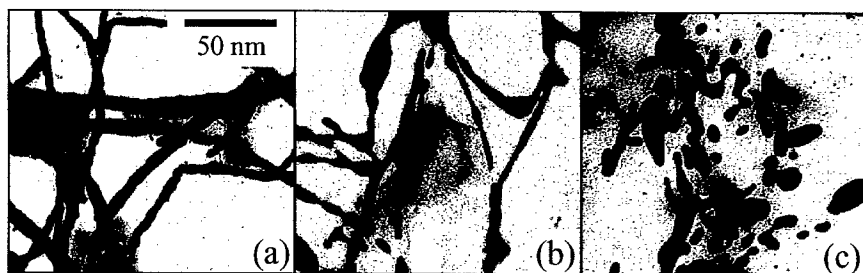
The TEM images of the freestanding Pd nanowires are shown in Figure 4a, 4b, and 4c. It was found that the diameters of the nanowires remain  $\sim 3.7$ ,  $\sim 4.6$ , and  $\sim 8.8$  nm which is consistent with the diameter of the nanowires encapsulated inside the matrix and remain unchanged after etching.



**Figure 4.** TEM images of the freestanding Pd nanowires after removal of the silica matrices: obtained from (a)  $C_{16}$ MCM-41 template, (b)  $C_{22}$ MCM-41 template, (c) SBA-15 template.

The lengths of the matrix free Pd nanowires also vary from 50 to a few hundred nanometers as they did inside the matrix channels. Selected-area electron diffraction patterns of the Pd nanowires exhibit the (111), (220), and (311) directions and confirms the cubic structure of polycrystalline Pd.

Figure 5 shows the thermal behavior of the 4.6 nm Pd nanowires. From room temperature to 150 °C, the nanowires are stable and essentially no changes is observed. However, the shape of the nanowires begin to deteriorate in certain areas of the wire at 200 °C. Finally, a large deformation and eventual collapse of the Pd nanowires in both width and shape is observed at 300 °C. Observed thermal behavior of the 4.6 nm Pd nanowires at 300 °C represents huge melting point depression of more than 1100 °C as compared to the bulk melting point of Pd at 1445 °C.



*Figure 5. Temperature dependent shape change of the ~4.6 nm Pd nanowires: (a) 150 °C, (b) 200 °C, (c) 300 °C.*

## CONCLUSION

In summary, this article demonstrates the size and shape-tuned synthesis of Pd nanowires and cages using hexagonal or cubic phased mesoporous silicate materials as templates via a CVI method. Combined results of XRD, TEM, EDAX, and XPS show that loaded Pd metal inside the silicate host materials do not affect the mesoporous silica framework, and uniquely structured Pd nanowires and cages without chemical contaminations and deformations are obtained after removal of the silica matrix HF. Our study indicates that mesoporous silica are good templates for the synthesis Pd nanostructured materials. A significantly depressed melting point of the Pd nanowires is observed around 300 °C due to large surface to volume ratio which is characteristic of nanomaterials. In addition, the low temperature CVI approach is of particular interest since the process conditions are mild enough to avoid any disruption of both the desired material and the template structure in the thermally sensitive nanoscale regime.

## ACKNOWLEDGMENT

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## Poster Session